



Cite this: *Dalton Trans.*, 2016, **45**, 4771

# Transition metal (Rh and Fe) complexes and main-group (Se and B) adducts with *N,N'*-diphosphanil NHC ligands: a study of stereoelectronic properties†

Pengfei Ai,<sup>a</sup> Andreas A. Danopoulos<sup>\*a,b</sup> and Pierre Braunstein<sup>\*a</sup>

Attempts to evaluate experimentally the donor characteristics of the *N,N'*-bis(di-*tert*-butylphosphanyl)-imidazole-2-ylidene (**PC<sub>NHC</sub>P**) hybrid ligand are described. Thus, reactions of **PC<sub>NHC</sub>P** with [Rh( $\mu$ -Cl)(COD)]<sub>2</sub> and [Rh( $\mu$ -Cl)(CO)<sub>2</sub>]<sub>2</sub> led to the formation of the mononuclear and dinuclear complexes, [Rh(**PC<sub>NHC</sub>P**, $\kappa$ P, $\kappa$ C<sub>NHC</sub>)<sub>2</sub>]Cl (**PC<sub>NHC</sub>P**-RhCl) and [Rh(CO)(**PC<sub>NHC</sub>P**, $\kappa$ P, $\kappa$ C<sub>NHC</sub>, $\kappa$ N)]<sub>2</sub> (**PC<sub>NHC</sub>P**-RhCO), respectively, the latter resulting after *in situ* cleavage of one (t-Bu)<sub>2</sub>P–N<sub>imid</sub> bond of **PC<sub>NHC</sub>P**. With ligands acting as a P,C-chelate, a straightforward evaluation of the Tolman electronic parameter (TEP) of the C<sub>NHC</sub> donor is problematical; the viability of dangling P- and bound C<sub>NHC</sub>-donors (*i.e.*  $\kappa$ C<sub>NHC</sub>) has been observed in the trinuclear Fe(II) chain complex [Fe<sub>3</sub>Cl<sub>2</sub>( $\mu$ -Cl)<sub>4</sub>(THF)<sub>2</sub>(**PC<sub>NHC</sub>P**, $\kappa$ C<sub>NHC</sub>)<sub>2</sub>] (**PC<sub>NHC</sub>P**-Fe), obtained by the reaction of **PC<sub>NHC</sub>P** with [Fe<sub>3</sub>Cl<sub>2</sub>(THF)<sub>6</sub>] and, recently, established on Cr<sup>II</sup>, Co<sup>II</sup> and Au<sup>I</sup> centres. Evaluation of the  $\pi$ -accepting properties of the **PC<sub>NHC</sub>P** (and the related **Dipp-PC<sub>NHC</sub>**) was based on the <sup>77</sup>Se NMR chemical shifts of the corresponding NHC–Se adducts, **PC<sub>NHC</sub>P**-Se (and **Dipp-PC<sub>NHC</sub>**-Se), which were prepared from the free **PC<sub>NHC</sub>P** (and **Dipp-PC<sub>NHC</sub>**) and Se. The  $\pi$ -acidity of **PC<sub>NHC</sub>P** is found to be higher than that of **Dipp-PC<sub>NHC</sub>** but lower than that of **SIPr**. The donor ability of the C<sub>NHC</sub> in **PC<sub>NHC</sub>P** was explored by its reaction with the Lewis acids tris(pentafluorophenyl)borane (B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>) and tris(pentafluorophenyl)boroxine ([B(C<sub>6</sub>F<sub>5</sub>)BO]<sub>3</sub>), which resulted in stable donor–acceptor adducts with no FLP reactivity. The steric properties of **PC<sub>NHC</sub>P** and **Dipp-PC<sub>NHC</sub>** are conformation dependent, with the percent buried volume (%V<sub>bur</sub>) of **PC<sub>NHC</sub>P** in the structurally characterised conformer calculated at 67.6, the largest value currently reported for NHC ligands.

Received 22nd January 2016,

Accepted 2nd February 2016

DOI: 10.1039/c6dt00318d

www.rsc.org/dalton

## Introduction

N-heterocyclic carbene (NHC) ligands have become ubiquitous in molecular chemistry and find extensive applications in *e.g.* catalytic transformations, medicinal chemistry and material sciences.<sup>1</sup> Both experimental and theoretical studies on their electronic properties have established synergism resulting from their strong  $\sigma$  donor and weaker  $\pi$  acceptor properties. The most commonly used method for the experimental evaluation of the donor properties of NHCs is the Tolman electronic parameter (TEP), originally developed for phosphines by Tolman in 1970,<sup>2</sup> which is based on the value of the A<sub>1</sub>  $\nu$ (CO) infrared-stretching frequencies in [Ni(CO)<sub>3</sub>L], or the average

$\nu$ (CO) frequencies in *cis*-[Ir(CO)<sub>2</sub>ClL] and *cis*-[Rh(CO)<sub>2</sub>ClL] (Chart 1), the latter two complexes being more widely used nowadays owing to the toxicity of [Ni(CO)<sub>4</sub>].<sup>2,3</sup> However, the TEP quantifies the overall NHC electronic properties and does not separate the  $\sigma$  donation and  $\pi$  back-donation components.

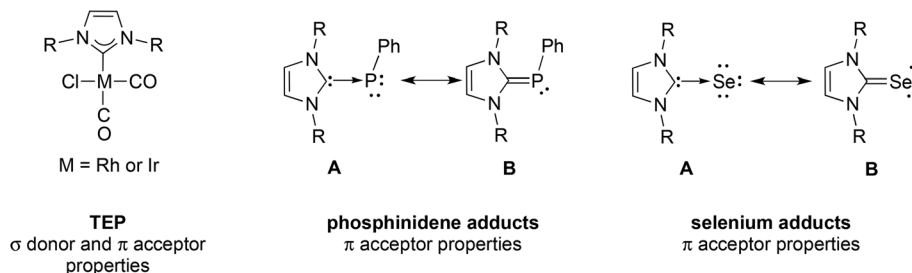
Recently, Bertrand and coll.<sup>4</sup> and Ganter and coll.<sup>5</sup> separately reported the use of phosphinidene (NHC)PPh and selenium adducts (NHC)Se (Chart 1) to probe the NHC  $\pi$  back-bonding ability, on the basis of the  $\delta_p$  chemical shift in the <sup>31</sup>P NMR and the  $\delta_{se}$  chemical shift in the <sup>77</sup>Se NMR, respectively. These adducts can be represented by two limiting canonical structures: the polarized form **A** with a NHC–E (E = PPh or Se) single bond indicating little  $\pi$  accepting ability and the resonance form **B** with a NHC–E (E = PPh or Se) double bond consistent with a high  $\pi$  accepting ability of NHCs. In contrast to the narrow range of TEP values, the chemical shifts of the phosphinidene/selenium adducts are very sensitive to subtle changes of the electronic structures of NHCs and offer a finer grading of the NHCs.

Various groups have recently reported *N*-phosphanil-functionalized NHC ligands, which feature the two adjacent, strong  $\sigma$ -donors groups linked by a direct P–N bond.<sup>6</sup> Because of the

<sup>a</sup>Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 4 rue Blaise Pascal, 67081 Strasbourg Cedex, France. E-mail: danopoulos@unistra.fr, braunstein@unistra.fr

<sup>b</sup>Institute for Advanced Study, USIAS, Université de Strasbourg, France

†Electronic supplementary information (ESI) available: Crystal data for **PCP**-RhCl-2CH<sub>2</sub>Cl<sub>2</sub>, **PC<sub>NHC</sub>**-RhCO, **PC<sub>NHC</sub>**-P-Fe, **PC<sub>NHC</sub>**-P-Se, **PC<sub>NHC</sub>**-P-B1-THF and **PC<sub>NHC</sub>**-P-B2-toluene. CCDC 1449234–1449239. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt00318d



**Chart 1** Three experimental methods used to evaluate the electronic properties of NHC ligands.

rigidity and ease of tuning of their steric and electronic properties, they have not only been used as bridging ligands for  $d^{10}$  coinage metals but also as small bite angle (*ca.* 68.2°) chelating ligands for platinum group or late transition metals.<sup>6c-f,7</sup>

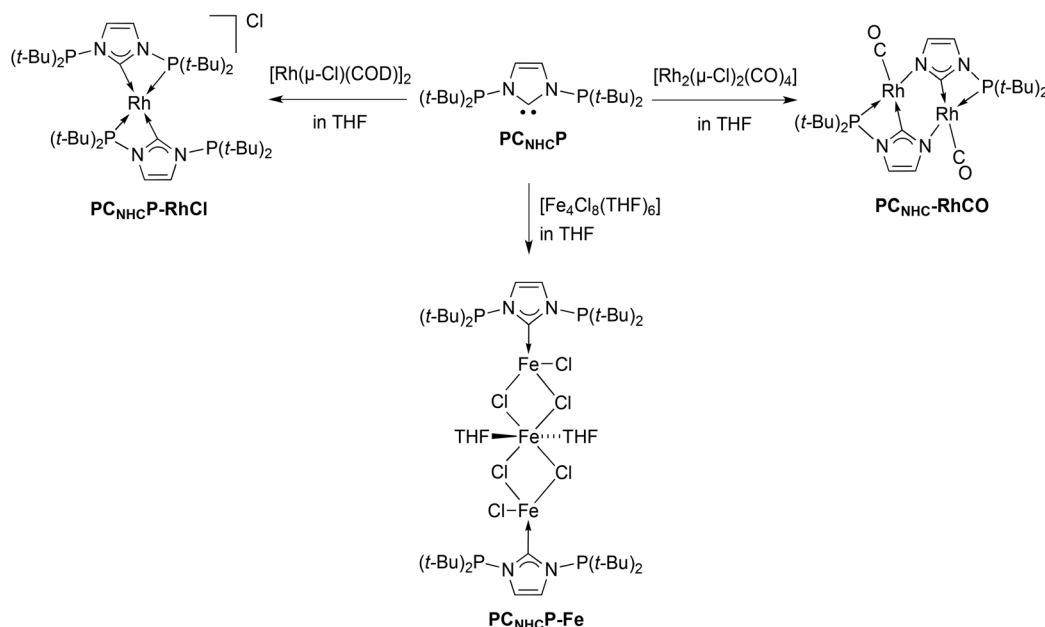
We have recently reported the synthesis of the new tridentate ligand *N,N'*-bis(di-*tert*-butylphosphanyl)-imidazole-2-ylidene (**PC<sub>NHC</sub>P**) (Scheme 1) and its behaviour as bridging ligand with coinage metals or palladium, resulting in polynuclear complexes,<sup>6h,i,8</sup> and as **PC<sub>NHC</sub>** chelating ligand with chromium or palladium.<sup>8a,9</sup> However, a more precise experimental estimate of the stereoelectronic properties of C<sub>NHC</sub> donor in the **PC<sub>NHC</sub>P** ligand is not straightforward, due to the high nucleophilicity of both donors and the propensity of formation of small ring chelates with the metals used as probes for the TEP. Herein, we describe Rh(I) carbonyl complexes with **PC<sub>NHC</sub>P** which display  $\kappa P, \kappa C_{NHC}$  coordination, thus rendering the evaluation of the TEP cumbersome; in contrast, the selective access of NHC–Se adducts permits the evaluation of the  $\pi$  accepting ability of the C<sub>NHC</sub> in **PC<sub>NHC</sub>P**; furthermore we give an estimate of the steric bulk of **PC<sub>NHC</sub>P**, and describe adducts with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and FeCl<sub>2</sub> in which C<sub>NHC</sub> coordination predominates.

## Results and discussion

### Mono- and dinuclear rhodium complexes and trinuclear iron complex

Since no rhodium complex with the **PC<sub>NHC</sub>P** has yet been prepared, with the objective to prepare *cis*-[RhCl(CO)<sub>2</sub>(**PC<sub>NHC</sub>P**)] we firstly reacted **PC<sub>NHC</sub>P** with [Rh( $\mu$ -Cl)(COD)]<sub>2</sub> in THF in a 1:1 ligand/Rh ratio (Scheme 1). However, instead of the expected adduct [RhCl(COD)(**PC<sub>NHC</sub>P**,  $\kappa C_{NHC}$ )], the mononuclear complex [Rh(**PC<sub>NHC</sub>P**,  $\kappa P, \kappa C_{NHC}$ )<sub>2</sub>]Cl (**PC<sub>NHC</sub>P**-RhCl) was isolated, the two **PC<sub>NHC</sub>P** ligands acting as P,C-chelates. This was confirmed by single-crystal X-ray diffraction analysis (Fig. 1).

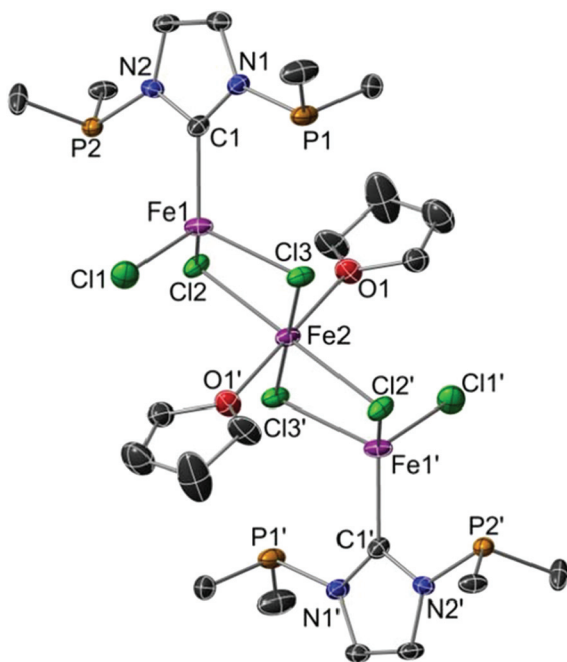
The unit cell of **PC<sub>NHC</sub>P**-RhCl contains two similar complex cations with slightly different metrical data and isolated chloride anions (Rh–Cl distance 7.418/7.359 Å). In each cation, the tetracoordinated Rh atom occupies a centre of symmetry and is chelated by two **PC<sub>NHC</sub>P** ligands through their C<sub>NHC</sub> and one phosphorus donor, with a bite angle of 67.26(11)/67.31(13)°. The solution <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **PC<sub>NHC</sub>P**-RhCl contains a doublet at  $\delta$  113.1 (<sup>1</sup>J(P–Rh) = 146.9 Hz) and a singlet at  $\delta$  83.8,



**Scheme 1** Reactions of **PC<sub>NHC</sub>P** with [Rh( $\mu$ -Cl)(COD)]<sub>2</sub>, [Rh( $\mu$ -Cl)(CO)<sub>2</sub>]<sub>2</sub> and [Fe<sub>4</sub>Cl<sub>8</sub>(THF)<sub>6</sub>].

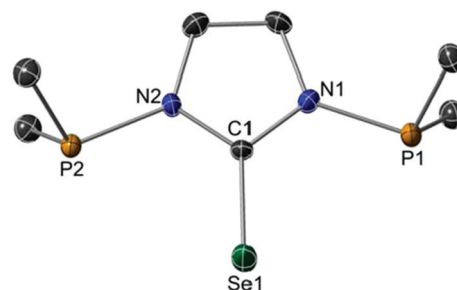






**Fig. 3** Thermal ellipsoid representation (30% probability level) of the structure of  $\text{PC}_{\text{NHC}}\text{P-Fe}$ . H atoms and the *t*-Bu methyl groups are omitted for clarity. Selected bond lengths (Å) and angles [°]: Fe1–C1 2.103(6), Fe1–Cl1 2.2587(19), Fe1–Cl2 2.3807(17), Fe1–Cl3 2.4118(18), Fe2–Cl2 2.4781(14), Fe2–Cl3 2.4755(14), Fe2–O1 2.158(4); Fe1–Cl2–Fe2 91.98(5), Fe1–Cl3–Fe2 91.30(5), C1–Fe1–Cl1 112.98(16), C1–Fe1–Cl2 115.81(15), C1–Fe1–Cl3 115.31(16), Cl1–Fe1–Cl2 111.90(7), Cl1–Fe1–Cl3 109.59(6), Cl2–Fe1–Cl3 88.99(6), O1–Fe2–Cl3' 88.33(11).

The second attempt focused on the synthesis of selenium adducts; herein, the  $\pi$ -accepting properties of NHCs precursors can also be correlated with the  $^{77}\text{Se}$  NMR chemical shift observed.<sup>5</sup> Thus, reaction of elemental selenium with  $\text{PC}_{\text{NHC}}\text{P}$  in a 1 : 1 ratio in THF afforded selectively the desired adduct  $\text{PC}_{\text{NHC}}\text{P-Se}$ , with intact phosphine groups (Scheme 2), as indicated by a  $^{31}\text{P}$  NMR shift (s,  $\delta$  91.0) (*cf.*  $\text{PC}_{\text{NHC}}\text{P}$   $\delta$  s, 98.7). The structure of the product was further confirmed by an X-ray diffraction analysis (Fig. 4). The Se–C<sub>NHC</sub> bond distance 1.839(8) Å is intermediate between that of a Se–C single bond (aver. 1.94 Å) and of a typical Se=C double bond (aver. 1.74 Å).<sup>12</sup> Its value is similar to that found in other selenium–NHC adducts.<sup>5b,12a–c</sup> Compared to the free carbene  $\text{PC}_{\text{NHC}}\text{P}$ , the



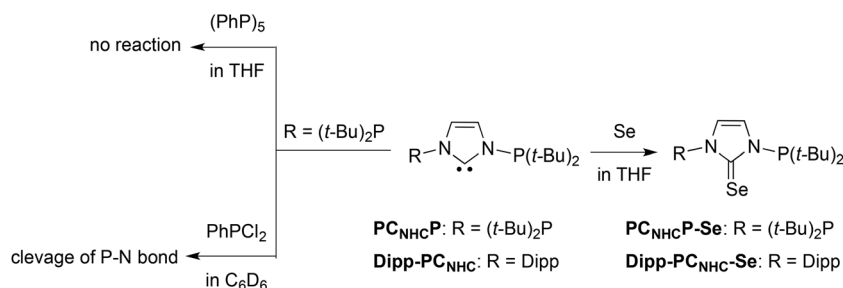
**Fig. 4** Thermal ellipsoid representation (30% probability level) of the structure of  $\text{PC}_{\text{NHC}}\text{P-Se}$ . H atoms and the *t*-Bu methyl groups are omitted for clarity. Selected bond lengths (Å) and angles [°]: C1–Se1 1.839(8), C1–N1 1.36(1), C1–N2 1.370(9), N1–P1 1.760(7), N2–P2 1.775(7); N1–C1–N2 108.2(6).

N–C<sub>NHC</sub> bond lengths (1.36(1)/1.370(9) Å, *cf.* 1.376(1)/1.378(1) Å in  $\text{PC}_{\text{NHC}}\text{P}$ ) are shortened and the N1–C1–N2 angle (108.2(6)°, *cf.* 102.5(1)° in  $\text{PC}_{\text{NHC}}\text{P}$ ) enlarged.

For comparison with  $\text{PC}_{\text{NHC}}\text{P-Se}$ , the selenium adduct **Dipp-PC<sub>NHC</sub>-Se** of a ligand containing only one phosphine group was prepared under similar reaction conditions (Scheme 2). The  $^{77}\text{Se}$  NMR spectra feature a triplet at  $\delta$  166.9 ( $^2J_{\text{SeP}} = 46.5$  Hz) for  $\text{PC}_{\text{NHC}}\text{P-Se}$  and a doublet at  $\delta$  131.1 ( $^2J_{\text{SeP}} = 40.0$  Hz) for **Dipp-PC<sub>NHC</sub>-Se**. Accordingly, and by comparison with literature data, it can be concluded that the  $\pi$ -acidity of  $\text{PC}_{\text{NHC}}\text{P}$  is stronger than that of **Dipp-PC<sub>NHC</sub>** and that both ligands are stronger  $\pi$ -acids than **SIMes** ( $\delta$  110  $^{77}\text{Se}$  NMR), but weaker  $\pi$ -acids than **SIPr** ( $\delta$  190  $^{77}\text{Se}$  NMR) (Scheme 3).<sup>13</sup>

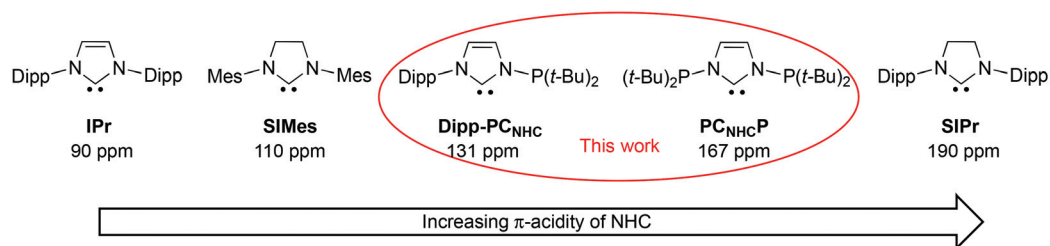
To further explore the donor abilities of the C<sub>NHC</sub> and P donors in  $\text{PC}_{\text{NHC}}\text{P}$ , the latter was reacted with tris(pentafluorophenyl)borane  $\text{B}(\text{C}_6\text{F}_5)_3$  in toluene (Scheme 4). The  $^{11}\text{B}$  NMR spectrum of the resulting product (**PC<sub>NHC</sub>P-B1**) shows a single resonance at  $\delta$  –17.5, which is indicative of a four-coordinate boron centre and suggests the formation of a NHC–borane Lewis adduct with a stable B–C<sub>NHC</sub> bond.

Broad NMR resonances were not only observed for the three pentafluorophenyl groups in the  $^{19}\text{F}$  NMR and  $^{13}\text{C}$  NMR spectra but also for the phosphine groups (one broad singlet at  $\delta$  110.5) and C<sub>NHC</sub> (broad multiplet at  $\delta$  177.1). This, together with the singlet at  $\delta$  7.69 for the two protons on the imidazolylidene ring, indicates fast free rotation of the  $\text{B}(\text{C}_6\text{F}_5)_3$  moiety around the B–C<sub>NHC</sub> bond. A single-crystal

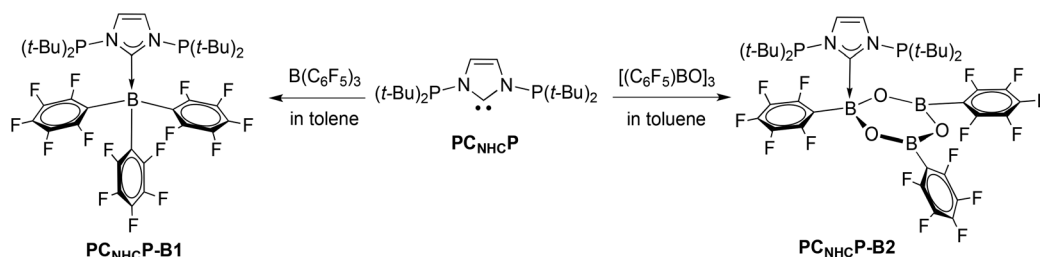


**Scheme 2** Reactions of  $\text{PC}_{\text{NHC}}\text{P}$  and **DIPP-PC<sub>NHC</sub>** with  $\text{PhPCl}_2$ ,  $(\text{PhP})_5$  and elemental selenium.





**Scheme 3** Comparative  $\pi$ -acidity of NHC ligands based on the  $^{77}\text{Se}$  NMR data (in  $\text{CDCl}_3$ ).



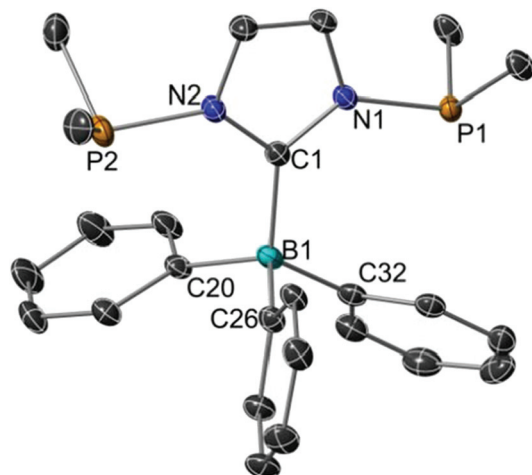
**Scheme 4** Synthesis of the adducts  $\text{PC}_{\text{NHC}}\text{P-B-1}$  and  $\text{PC}_{\text{NHC}}\text{P-B-2}$ .

X-ray diffraction analysis showed that the three  $\text{C}_6\text{F}_5$  groups adopt a typical  $C_3$  propeller-type orientation (Fig. 5). For steric reasons, the lone pair on the P atoms is oriented toward the borane moiety.

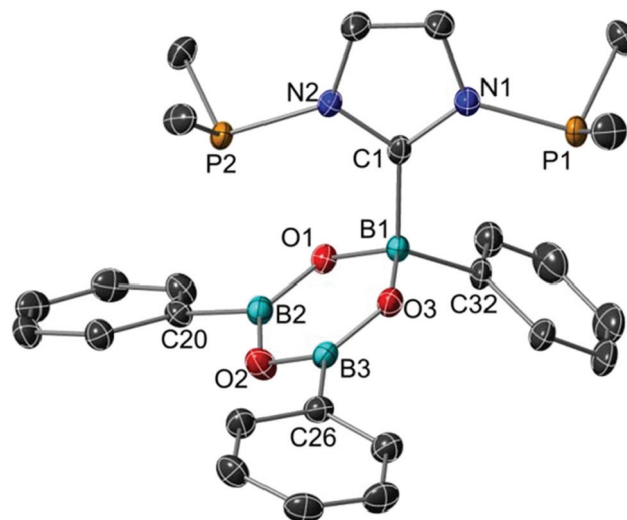
Unlike other NHC–borane adducts,<sup>14</sup>  $\text{PC}_{\text{NHC}}\text{P-B-1}$  exhibits no frustrated-Lewis-pair (FLP) reactivity toward  $\text{H}_2$  or THF, which is consistent with a rather strong donor–acceptor  $\text{C}_{\text{NHC}} \rightarrow \text{B}$  interaction, despite a moderate elongation of this bond (1.688(3) Å) when compared to that in the adduct  $\text{IPr/B(C}_6\text{F}_5)_3$

(1.663(5) Å)<sup>14a</sup> and in 1,3,4,5-tetramethyl-1,3-imidazole-2-ylidene/ $\text{B(C}_6\text{F}_5)_3$  (1.640(2) Å).<sup>15</sup>

Another donor–acceptor adduct was obtained by reaction of  $\text{PC}_{\text{NHC}}\text{P}$  with a suspension of tris(pentafluorophenyl)boroxine  $[(\text{C}_6\text{F}_5)\text{BO}]_3$  in toluene (Scheme 4). An immediate reaction occurred with formation of a clear solution. A crystallographic analysis established again the formation of one  $\text{C}_{\text{NHC}} \rightarrow \text{B}$  bond in the boroxine adduct  $\text{PC}_{\text{NHC}}\text{P-B-2}$ , leaving the other two B atoms intact (Fig. 6). The  $\text{B-C}_{\text{NHC}}$  bond distance 1.670(4) Å



**Fig. 5** Thermal ellipsoid representation (30% probability level) of the structure of  $\text{PCP-B-1}$ . H atoms, the *t*-Bu methyl groups, all the F atoms and one molecule of THF are omitted for clarity. Selected bond lengths (Å) and angles [°]: B1–C1 1.688(3), B1–C20 1.659(3), B1–C26 1.660(3), B1–C32 1.670(3), N1–C1–N2 104.98(15), C20–B1–C26 111.11(16), C20–B1–C32 112.03(16), C26–B1–C32 101.70(15), C20–B1–C1 106.09(15), C26–B1–C1 110.95(16), C32–B1–C1 115.06(15).



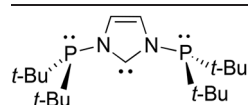
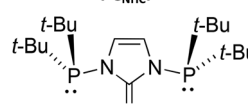
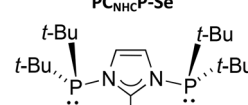
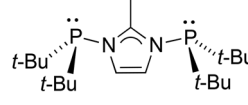
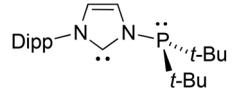
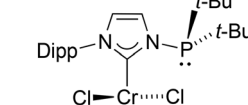
**Fig. 6** Thermal ellipsoid representation (30% probability level) of the structure of  $\text{PC}_{\text{NHC}}\text{P-B-2}$ . H atoms, the *t*-Bu methyl groups, all the F atoms and one molecule of toluene are omitted for clarity. Selected bond lengths (Å) and angles [°]: C1–B1 1.670(4), C20–B2 1.590(4), C26–B3 1.586(4), C32–B1 1.643(4), N1–C1–N2 105.6(2), O1–B1–C1 108.6(2), O3–B1–C1 105.0(2), C32–B1–C1 113.7(2).



is slightly shorter than that in **PC<sub>NHC</sub>P-B1**. Obvious differences were observed between the three B–C<sub>6</sub>F<sub>5</sub> moieties: (i) the B1–C32 bond (1.643(4) Å) is elongated compared to the other two (1.590(4) Å and 1.586(4) Å); (ii) the B2–C20 and B3–C26 bonds are coplanar with the boroxine ring while the B1–C32 bond bends out of the boroxine plane, away from the **PC<sub>NHC</sub>P** ligand with a distance of 1.393 Å between the C23 atom and the boroxine plane. This results from the coordination of B1 to C<sub>NHC</sub> forming a tetrahedral environment around the B1 atom.

The <sup>31</sup>P NMR spectrum shows one singlet at δ 97.6 for the phosphine groups and a doublet is observed in the <sup>1</sup>H NMR spectrum at δ 1.15 (<sup>3</sup>J<sub>HP</sub> = 12.9 Hz) for the *t*-Bu groups, which indicates free rotation of the boroxine moiety around the B–C<sub>NHC</sub> bond. The <sup>11</sup>B NMR spectrum contains a broad signal at δ 26.4 and a singlet at δ –0.6 ppm corresponding to the three- and four-coordinate B atoms, respectively. Similarly to **PC<sub>NHC</sub>P-B1**, it exhibited no frustrated-Lewis-pair (FLP) reactivity toward H<sub>2</sub> or THF.

Table 1 Percent buried volume (%V<sub>bur</sub>)

Compounds	%V <sub>bur</sub> for M–NHC length at	
	2.00 Å	2.28 Å
 <b>PC<sub>NHC</sub>P</b>	67.6	63.1
 <b>PC<sub>NHC</sub>P-Se</b>	32.5	28.3
 <b>PC<sub>NHC</sub>P-Kr</b>	36.4	31.7
 <b>[CrCl<sub>2</sub>(PC<sub>NHC</sub>P-KrC<sub>NHC</sub>)<sub>2</sub>]<sup>9</sup></b>	39.4	36.2
 <b>Dipp-PC<sub>NHC</sub></b>	35.8	31.0
 <b>[CrCl<sub>2</sub>(Dipp-PC<sub>NHC</sub>-KrC<sub>NHC</sub>)<sub>2</sub>]<sup>9</sup></b>		

## Percent buried volume of the NHC ligands

Lastly, the steric properties of **PC<sub>NHC</sub>P** and **Dipp-PC<sub>NHC</sub>** were evaluated from the percent buried volume (%V<sub>bur</sub>) using the SambVca software,<sup>16</sup> and metrical data from the crystal structures. The results are compiled in Table 1 assuming a 3.50 Å for the sphere radius, omitted hydrogen atoms and scaled bond radii by 1.17, as recommended. Rotation of the phosphine group around the P–N bond has dramatic effect on the steric environment at the carbene centre, especially for **PC<sub>NHC</sub>P**. The %V<sub>bur</sub> of the free carbene **PC<sub>NHC</sub>P** reaches a value up to 67.6 (M–NHC 2.00 Å), for the conformation observed crystallographically, featuring *anti* lone pair arrangement; this value is the largest value among all reported NHC ligands (Table 1).<sup>17</sup> In the conformation with *syn* arrangement of the lone pairs which is commonly found on κC<sub>NHC</sub> coordination or adduct formation the %V<sub>bur</sub> decreases to 32.5 for **PC<sub>NHC</sub>P-Se** and 36.4 for [CrCl<sub>2</sub>(PC<sub>NHC</sub>P-κC<sub>NHC</sub>)<sub>2</sub>]<sup>9</sup> (M–NHC 2.00 Å). Compared to the %V<sub>bur</sub> values found in **PC<sub>NHC</sub>P**, that for **Dipp-PC<sub>NHC</sub>** is smaller (39.4, M–NHC 2.00 Å) but similar (35.8, M–NHC 2.00 Å) to that in the Cr(II) complexes.

## Conclusions

Some stereoelectronic properties of the hybrid ligands **PC<sub>NHC</sub>P** and **Dipp-PC<sub>NHC</sub>** have been evaluated. Initial attempts to prepare *cis*-[RhCl(CO)<sub>2</sub>(PC<sub>NHC</sub>P-κC<sub>NHC</sub>)] by the reaction of **PC<sub>NHC</sub>P** with [Rh(μ-Cl)(COD)]<sub>2</sub> or [Rh(μ-Cl)(CO)<sub>2</sub>]<sub>2</sub> led instead to the formation of rhodium complexes with a chelating PC<sub>NHC</sub>P,κP,κC<sub>NHC</sub> or PC<sub>NHC</sub>,κP,κC<sub>NHC</sub>,κN ligand, and the additional coordination of the phosphine group hampered the evaluation of the TEP of the sole C<sub>NHC</sub> donor. However, the π-accepting properties of **PC<sub>NHC</sub>P** and **Dipp-PC<sub>NHC</sub>** were determined from the <sup>77</sup>Se NMR chemical shift of the corresponding selenium adducts. The σ-donor ability of the carbene donor in **PC<sub>NHC</sub>P** was confirmed by the isolation of two stable donor-acceptor adducts with borane or boroxine. The free carbene donor of **PC<sub>NHC</sub>P** shows the largest value reported for percent buried volume in NHC ligands in the conformation of the free **PC<sub>NHC</sub>P** established crystallographically. Currently, it appears that a coordination mode through the C<sub>NHC</sub> donor (κC<sub>NHC</sub>) is more common with 3d metals.

## Experimental section

### Synthesis and characterisation

**General methods.** All manipulations involving organometallics were performed under argon using standard Schlenk techniques. Solvents were dried using standard methods and distilled under nitrogen prior to use or passed through columns of activated alumina and subsequently purged with nitrogen or argon. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded at 298 K, unless otherwise specified, on a Bruker Avance 400, 500 or 600 spectrometer and referenced to the residual solvent resonance (<sup>1</sup>H and <sup>13</sup>C) or external 85% H<sub>3</sub>PO<sub>4</sub>.



in D<sub>2</sub>O (<sup>31</sup>P). The <sup>77</sup>Se NMR spectra were referenced to external KSeCN in D<sub>2</sub>O at a specific concentration with a chemical shift of −329.0 ppm (0.25 mol L<sup>−1</sup>). Abbreviation used are s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, dd = doublet of doublets, ddt = doublet of doublet of triplets, dm = doublet of multiplets, br = broad, br d = broad doublet, br m = broad multiplet. Elemental analyses were performed by the “Service de microanalyses”, Université de Strasbourg. The preparations of **PC<sub>NHC</sub>P** and **Dipp-PC<sub>NHC</sub>** have been reported before.<sup>6f,h</sup> The precursors [Rh(μ-Cl)(COD)]<sub>2</sub>,<sup>18</sup> [Rh<sub>2</sub>(μ-Cl)Cl(CO)<sub>4</sub>],<sup>19</sup> [(C<sub>6</sub>F<sub>5</sub>)BO]<sub>3</sub>,<sup>20</sup> and [Fe<sub>4</sub>Cl<sub>8</sub>(THF)<sub>6</sub>]<sup>21</sup> were prepared according to the literature.

**Synthesis of PC<sub>NHC</sub>P-RhCl.** To a solution of [RhCl(COD)]<sub>2</sub> (0.030 g, 0.061 mmol) in THF (5 ml) was added a solution of **PC<sub>NHC</sub>P** (0.100 g, 0.281 mmol) in THF (5 ml) at room temperature and the reaction mixture was stirred for 2 h. After evaporation of the volatiles, the residue was washed with pentane (20 ml) and dried under vacuum to give a bright yellow powder (0.100 g, 96%). X-ray quality crystals were obtained by slow diffusion of pentane into its CH<sub>2</sub>Cl<sub>2</sub> solution. Analysis: Found (Calcd for C<sub>38</sub>H<sub>76</sub>ClN<sub>4</sub>P<sub>4</sub>Rh) (%): C, 53.57 (53.61), H, 8.89 (9.00), N, 6.75 (6.58). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.15 (d, 2H, <sup>3</sup>J<sub>HP</sub> = 2.1 Hz, im-*H*), 7.13 (s, 2H, im-*H*), 1.52 (t, 36H, <sup>3</sup>J<sub>HP</sub> = 7.4 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.21 (d, 36H, <sup>3</sup>J<sub>HP</sub> = 12.5 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 186.1 (ddt, <sup>2</sup>J<sub>CP</sub> = 53.5 Hz, <sup>1</sup>J<sub>C-Rh</sub> = 40.4 Hz, <sup>2</sup>J<sub>CP</sub> = 11.2 Hz, NCN), 124.2 (d, <sup>2</sup>J<sub>CP</sub> = 6.5 Hz, im-*C*), 122.2 (im-*C*), 36.8 (q, <sup>1</sup>J<sub>CP</sub> = 2.0 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 35.2 (d, <sup>1</sup>J<sub>CP</sub> = 29.6 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 29.5 (q, <sup>2</sup>J<sub>CP</sub> = 4.5 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 29.1 (d, <sup>2</sup>J<sub>CP</sub> = 15.7 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 113.1 (d, <sup>1</sup>J<sub>P-Rh</sub> = 146.9 Hz), 83.8 (s).

**Synthesis of PC<sub>NHC</sub>P-RhCO.** To a solution of [Rh<sub>2</sub>(μ-Cl)<sub>2</sub>(CO)<sub>4</sub>] (0.088 g, 0.226 mmol) in THF (5 ml) was added a solution of **PC<sub>NHC</sub>P** (0.160 g, 0.449 mmol) in THF (5 ml) at room temperature and the reaction mixture was stirred for 2 h. It was then concentrated to ca. 2 ml and 20 ml pentane were added to precipitate the product. The supernatant was removed by filtration and the solid was dried under vacuum to give a brown powder (0.066 g, 44%). X-ray quality crystals were obtained by slow diffusion of pentane into its THF solution. Analysis: Found (Calcd for C<sub>24</sub>H<sub>40</sub>O<sub>2</sub>N<sub>4</sub>P<sub>2</sub>Rh<sub>2</sub>) (%): C, 42.01 (42.12), H, 5.79 (5.89), N, 8.43 (8.19). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.04 (t, 2H, <sup>3</sup>J<sub>HP</sub> = 1.8 Hz, im-*H*), 6.95 (s, 2H, im-*H*), 1.40 (d, 36H, <sup>3</sup>J<sub>HP</sub> = 15.0 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 194.09 (dd, <sup>1</sup>J<sub>C-Rh</sub> = 61.9 Hz, <sup>2</sup>J<sub>CP</sub> = 12.9 Hz, CO), 177.3 (dd, <sup>1</sup>J<sub>C-Rh</sub> = 35.8 Hz, <sup>2</sup>J<sub>CP</sub> = 24.2 Hz, NCN), 132.3 (d, <sup>3</sup>J<sub>CP</sub> = 5.3 Hz, im-*C*), 119.4 (d, <sup>2</sup>J<sub>CP</sub> = 7.0 Hz, im-*C*), 37.1 (d, <sup>1</sup>J<sub>CP</sub> = 10.3 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 28.4 (d, <sup>2</sup>J<sub>CP</sub> = 6.6 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 128.4 (d, <sup>1</sup>J<sub>Rh-P</sub> = 142.8 Hz).

**Synthesis of PC<sub>NHC</sub>P-Fe.** In the glovebox, 2 ml THF was added at room temperature to a solid mixture of **PC<sub>NHC</sub>P** (0.020 g, 0.056 mmol) and [Fe<sub>4</sub>Cl<sub>8</sub>(THF)<sub>6</sub>] (0.012 g, 0.013 mmol). After it was stirred for 0.5 h, the solution was layered with 10 ml pentane and crystallization for four days yielded colourless and extremely air-sensitive crystals (0.014 g, 67%), which were suitable for X-ray diffraction. Due to the air sensitivity of this complex, satisfactory elemental analyses could not be obtained.

**Synthesis of PC<sub>NHC</sub>P-Se.** To a solution of **PC<sub>NHC</sub>P** (0.050 g, 0.140 mmol) in THF (5 ml) was added a suspension of selenium (0.011 g, 0.139 mmol) in THF (8 ml) at room temperature and the reaction mixture was stirred for 1 h. After evaporation of the solvent to dryness, the residue was washed with pentane (10 ml) and dried under vacuum to give a white powder (0.057 g, 93%). X-ray quality crystals were obtained by slow diffusion of pentane into its THF solution at −30 °C. Analysis: Found (Calcd for C<sub>19</sub>H<sub>38</sub>N<sub>2</sub>P<sub>2</sub>Se) (%): C, 52.30 (52.41), H, 8.78 (8.80), N, 6.73 (6.43). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.19 (s, im-*H*), 1.25 (d, 36H, <sup>3</sup>J<sub>HP</sub> = 12.4 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.18 (s, im-*H*), 1.22 (d, 36H, <sup>3</sup>J<sub>HP</sub> = 12.3 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 176.6 (t, <sup>2</sup>J<sub>CP</sub> = 34.3 Hz, NCN), 122.6 (t, <sup>2</sup>J<sub>CP</sub> = 4.3 Hz, im-*C*), 35.9 (d, <sup>1</sup>J<sub>CP</sub> = 33.7 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 29.3 (d, <sup>2</sup>J<sub>CP</sub> = 17.7 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, CDCl<sub>3</sub>): δ 91.0 (s). <sup>77</sup>Se NMR (114 MHz, CDCl<sub>3</sub>): δ 166.9 (t, <sup>2</sup>J<sub>SeP</sub> = 46.5 Hz).

**Synthesis of Dipp-PC<sub>NHC</sub>-Se.** A synthetic procedure similar to that for **PC<sub>NHC</sub>P-Se** was applied using **Dipp-PC<sub>NHC</sub>** (0.050 g, 0.134 mmol) and selenium (0.010 g, 0.127 mmol). Compound **Dipp-PC<sub>NHC</sub>-Se** was obtained as a white powder (0.055 g, 92%). Analysis: Found (Calcd for C<sub>23</sub>H<sub>37</sub>N<sub>2</sub>PSe) (%): C, 61.01 (61.19), H, 8.20 (8.26), N, 6.41 (6.20). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.44 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, Ar-*H*), 7.31 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 2.1 Hz, <sup>4</sup>J<sub>HP</sub> = 0.3 Hz, im-*H*), 7.26 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, Ar-*H*), 6.87 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 2.1 Hz, <sup>3</sup>J<sub>HP</sub> = 1.3 Hz, im-*H*), 2.50 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, iPr-*CH*), 1.32 (d, 18H, <sup>3</sup>J<sub>HP</sub> = 12.5 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.28 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, iPr-*CH*<sub>3</sub>), 1.10 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, iPr-*CH*<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 169.1 (d, <sup>2</sup>J<sub>CP</sub> = 36.1 Hz, NCN), 146.1 (Ar-*C*), 134.9 (Ar-*C*), 130.2 (Ar-*CH*), 124.4 (Ar-*CH*), 122.0 (d, <sup>2</sup>J<sub>CP</sub> = 7.6 Hz, im-*C*), 121.7 (d, <sup>3</sup>J<sub>CP</sub> = 1.3 Hz, im-*C*), 35.9 (d, <sup>1</sup>J<sub>CP</sub> = 33.1 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 29.3 (d, <sup>2</sup>J<sub>CP</sub> = 17.5 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 29.0 (iPr-*CH*), 24.6 (iPr-*CH*<sub>3</sub>), 23.5 (iPr-*CH*<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, CDCl<sub>3</sub>): δ 90.5 (s). <sup>77</sup>Se NMR (114 MHz, CDCl<sub>3</sub>): δ 131.1 (d, <sup>2</sup>J<sub>SeP</sub> = 40.0 Hz).

**Synthesis of PC<sub>NHC</sub>P-B1.** To a solid mixture of free carbene **PC<sub>NHC</sub>P** (0.035 g, 0.098 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.051 g, 0.100 mmol) was added 3 ml toluene at room temperature and the reaction mixture was stirred for 2 h. After removal of the supernatant by filtration, the residue was washed with pentane (10 ml) and dried under reduced pressure to give a white powder (0.075 g, 87%). X-ray quality crystals were obtained by slow diffusion of pentane into its THF solution. Due to the sensitivity to air, satisfactory elemental analyses could not be obtained. <sup>1</sup>H NMR (400 MHz, *d*<sup>8</sup>-THF): δ 7.69 (s, 2H, im-*H*), 1.26 (d, 18H, <sup>3</sup>J<sub>HP</sub> = 13.1 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.01 (d, 18H, <sup>3</sup>J<sub>HP</sub> = 12.9 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, *d*<sup>8</sup>-THF): δ 177.1 (br m, NCN), 149.9 (br d, <sup>1</sup>J<sub>CF</sub> = 235.2 Hz, *o*-ArCF), 140.4 (br d, <sup>1</sup>J<sub>CF</sub> = 244.0 Hz, *p*-ArCF), 137.5 (br d, <sup>1</sup>J<sub>CF</sub> = 238.0 Hz, *m*-ArCF), 128.1 (im-*C*), 123.6 (br, ArCB), 37.0 (d, <sup>1</sup>J<sub>CP</sub> = 30.1 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 36.7 (d, <sup>1</sup>J<sub>CP</sub> = 31.1 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 29.4 (d, <sup>2</sup>J<sub>CP</sub> = 18.3 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 29.0 (d, <sup>2</sup>J<sub>CP</sub> = 18.5 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161 MHz, *d*<sup>8</sup>-THF): δ 110.5 (br). <sup>11</sup>B NMR (128 MHz, *d*<sup>8</sup>-THF): δ −17.5 (s). <sup>19</sup>F NMR (564 MHz, *d*<sup>8</sup>-THF): δ −122.0 (br, 2F, *o*-ArCF), −125.5 (br, 2F, *o*-ArCF), −132.1 (br, 2F, *o*-ArCF), −162.6 (br, 4F, *p*-ArCF), −168.2 (br, 2F, *m*-ArCF), −168.7 (br, 3F, *p*-ArCF), −169.1 (br, 2F, *m*-ArCF).



**Synthesis of PC<sub>NHC</sub>P-B2.** To a suspension of [(C<sub>6</sub>F<sub>5</sub>)BO]<sub>3</sub> (0.116 g, 0.199 mmol) in toluene (2 ml) was added a solution of PC<sub>NHC</sub>P (0.072 g, 0.202 mmol) in toluene (2 ml) at room temperature and stirring was maintained for 1 h. The reaction mixture was concentrated to 2 ml and 20 ml pentane was added to precipitate the product. After filtration, the residue was dried under reduced pressure to give a white powder (0.120 g, 64%). X-ray quality crystals were obtained by cooling down its toluene solution to −30 °C for two days. Analysis: Found (Calcd for C<sub>37</sub>H<sub>38</sub>B<sub>3</sub>F<sub>15</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>) (%): C, 47.72 (47.37), H, 4.17 (4.08), N, 2.97 (2.99). <sup>1</sup>H NMR (400 MHz, d<sup>8</sup>-THF): δ 7.66 (s, 2H, im-H), 1.15 (d, 36H, <sup>3</sup>J<sub>HP</sub> = 12.9 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, d<sup>8</sup>-THF): δ 175.9 (br, NCN), 149.9 (dm, <sup>1</sup>J<sub>CF</sub> = 249.7 Hz, o-ArCF), 148.7 (dm, <sup>1</sup>J<sub>CF</sub> = 241.6 Hz, o-ArCF-BC<sub>NHC</sub>), 142.8 (dm, <sup>1</sup>J<sub>CF</sub> = 255.3 Hz, p-ArCF), 140.3 (dm, <sup>1</sup>J<sub>CF</sub> = 241.4 Hz, p-ArCF-BC<sub>NHC</sub>), 137.8 (dm, <sup>1</sup>J<sub>CF</sub> = 250.7 Hz, overlapping m-ArCF and m-ArCF-BC<sub>NHC</sub>), 126.0 (im-C), 124.9 (br, ArCB), 109.7 (br, ArCB-C<sub>NHC</sub>), 35.9 (d, <sup>1</sup>J<sub>CP</sub> = 35.2 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 29.0 (d, <sup>2</sup>J<sub>CP</sub> = 17.7 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161 MHz, d<sup>8</sup>-THF): δ 97.6 (s). <sup>11</sup>B NMR (128 MHz, d<sup>8</sup>-THF): δ 26.4 (br, ArB), −0.6 (s, ArB-C<sub>NHC</sub>). <sup>19</sup>F NMR (282 MHz, d<sup>8</sup>-THF): δ −132.4 (dm, 4F, <sup>3</sup>J<sub>FF</sub> = 22.4 Hz, o-ArCF), −135.3 (m, 2F, o-ArCF-BC<sub>NHC</sub>), −156.0 (tt, 2F, <sup>3</sup>J<sub>FF</sub> = 20.0 Hz, <sup>4</sup>J<sub>FF</sub> = 3.1 Hz, p-ArCF), −164.0 (t, 1F, <sup>3</sup>J<sub>FF</sub> = 20.3 Hz, p-ArCF-BC<sub>NHC</sub>), −166.1 (m, 4F, m-ArCF), −168.5 (m, 2F, m-ArCF-BC<sub>NHC</sub>).

### X-ray crystallography

Summary of the crystal data, data collection and refinement for the structures of PCP-RhCl·2CH<sub>2</sub>Cl<sub>2</sub>, PC<sub>NHC</sub>-RhCO, PC<sub>NHC</sub>P-Fe, PC<sub>NHC</sub>P-Se, PC<sub>NHC</sub>P-B-1·THF and PC<sub>NHC</sub>P-B-2-toluene are given in Table S1.†

For PC<sub>NHC</sub>P-RhCl·2CH<sub>2</sub>Cl<sub>2</sub>, PC<sub>NHC</sub>P-Fe, PC<sub>NHC</sub>P-Se, PC<sub>NHC</sub>P-B-1·THF and PC<sub>NHC</sub>P-B-2-toluene, X-ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N<sub>2</sub> device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software)<sup>22</sup> from reflections taken from three sets of 12 frames, each at 10 s exposure. The structure was solved by direct methods using the program SHELXS-97.<sup>23</sup> The refinement and all further calculations were carried out using SHELXL-97.<sup>24</sup> The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F<sup>2</sup>. A semi-empirical absorption correction was applied using SADABS in APEX2.<sup>22</sup>

For PC<sub>NHC</sub>-RhCO, X-ray diffraction data collection was carried out on a Nonius Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N<sub>2</sub> device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 36 mm. The cell parameters were determined (Denzo software)<sup>25</sup> from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved by direct methods using the program SHELXS-97.<sup>23</sup> The refinement and all further calculations were carried out using

SHELXL-97.<sup>24</sup> The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F<sup>2</sup>. A semi-empirical absorption correction was applied using MULScanABS in PLATON.<sup>26</sup>

### Conflict of interest

The authors declare no competing financial interest.

### Acknowledgements

The USIAS, CNRS, Région Alsace and Communauté Urbaine de Strasbourg are acknowledged for the award of fellowships and a Gutenberg Excellence Chair (2010–11) to AAD. We thank the CNRS and the MESR (Paris) for funding and Dr L. Karmazin and Miss C. Bailly (Service de Radiocristallographie, UdS) for the determination of the crystal structures. We are grateful to the China Scholarship Council for a PhD grant to P.A.

### References

- (a) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; (b) C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247; (c) E. Peris and R. H. Crabtree, *Coord. Chem. Rev.*, 2004, **248**, 2239; (d) F. Glorius, *N-Heterocyclic Carbenes in Transition Metal Catalysis*, Springer, Berlin Heidelberg, 2007; (e) D. Pugh and A. A. Danopoulos, *Coord. Chem. Rev.*, 2007, **251**, 610; (f) E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem., Int. Ed.*, 2007, **46**, 2768; (g) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612; (h) D. McGuinness, *Dalton Trans.*, 2009, 6915; (i) K. Riener, S. Haslinger, A. Raba, M. P. Högerl, M. Cokoja, W. A. Herrmann and F. E. Kühn, *Chem. Rev.*, 2014, **114**, 5215; (j) R. Visbal and M. C. Gimeno, *Chem. Soc. Rev.*, 2014, **43**, 3551; (k) M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485; (l) Z. Wang, L. Jiang, D. K. B. Mohamed, J. Zhao and T. S. A. Hor, *Coord. Chem. Rev.*, 2015, **293–294**, 292; (m) D. Zhang and G. Zi, *Chem. Soc. Rev.*, 2015, **44**, 1898.
- C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
- D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, 2013, **42**, 6723.
- O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin and G. Bertrand, *Angew. Chem., Int. Ed.*, 2013, **52**, 2939.
- (a) A. Liske, K. Verlinden, H. Buhl, K. Schaper and C. Ganter, *Organometallics*, 2013, **32**, 5269; (b) K. Verlinden, H. Buhl, W. Frank and C. Ganter, *Eur. J. Inorg. Chem.*, 2015, **2015**, 2416.
- (a) A. P. Marchenko, H. N. Koidan, A. N. Huryeva, E. V. Zarudnitskii, A. A. Yurchenko and A. N. Kostyuk, *J. Org. Chem.*, 2010, **75**, 7141; (b) A. P. Marchenko,





- H. N. Koidan, I. I. Pervak, A. N. Huryeva, E. V. Zarudnitskii, A. A. Tolmachev and A. N. Kostyuk, *Tetrahedron Lett.*, 2012, **53**, 494; (c) A. P. Marchenko, H. N. Koidan, A. N. Huryeva, I. I. Pervak, S. V. Shishkina, O. V. Shishkin and A. N. Kostyuk, *Eur. J. Org. Chem.*, 2012, 4018; (d) A. P. Marchenko, H. N. Koidan, E. V. Zarudnitskii, A. N. Huryeva, A. A. Kirilchuk, A. A. Yurchenko, A. Biffis and A. N. Kostyuk, *Organometallics*, 2012, **31**, 8257; (e) A. Marchenko, H. Koidan, A. Huryeva, O. Kurpiieva, Y. Vlasenko, A. Kostyuk, C. Tubaro, A. Lenarda, A. Biffis and C. Graiff, *J. Organomet. Chem.*, 2014, **771**, 14; (f) P. Nägele, U. Herrlich, F. Rominger and P. Hofmann, *Organometallics*, 2013, **32**, 181; (g) T. Wang and D. W. Stephan, *Chem. – Eur. J.*, 2014, **20**, 3036; (h) P. Ai, A. A. Danopoulos, P. Braunstein and K. Y. Monakhov, *Chem. Commun.*, 2014, **50**, 103; (i) P. Ai, A. A. Danopoulos and P. Braunstein, *Inorg. Chem.*, 2015, **54**, 3722.
- 7 (a) A. P. Marchenko, H. N. Koidan, A. N. Huryeva, O. V. Gutov, A. N. Kostyuk, C. Tubaro, S. Lollo, A. Lanza, F. Nestola and A. Biffis, *Organometallics*, 2013, **32**, 718; (b) C. C. Brown, P. N. Plessow, F. Rominger, M. Limbach and P. Hofmann, *Organometallics*, 2014, **33**, 6754; (c) E. Kühnel, I. V. Shishkov, F. Rominger, T. Oeser and P. Hofmann, *Organometallics*, 2012, **31**, 8000.
- 8 (a) P. Ai, C. Gourlaouen, A. A. Danopoulos and P. Braunstein, *Inorg. Chem.*, 2016, **55**, 1219; (b) P. Ai, M. Mauro, L. De Cola, A. A. Danopoulos and P. Braunstein, *Angew. Chem., Int. Ed.*, 2016, DOI: 10.1002/anie.201510150.
- 9 P. Ai, A. A. Danopoulos and P. Braunstein, *Organometallics*, 2015, **34**, 4109.
- 10 F. He, L. Ruhlmann, J.-P. Gisselbrecht, S. Choua, M. Orio, M. Wesolek, A. A. Danopoulos and P. Braunstein, *Dalton Trans.*, 2015, **44**, 17030.
- 11 A. Massard, P. Braunstein, A. A. Danopoulos, S. Choua and P. Rabu, *Organometallics*, 2015, **34**, 2429.
- 12 (a) G. Roy, M. Nethaji and G. Mugesh, *J. Am. Chem. Soc.*, 2004, **126**, 2712; (b) G. Roy and G. Mugesh, *J. Am. Chem. Soc.*, 2005, **127**, 15207; (c) G. Roy, P. N. Jayaram and G. Mugesh, *Chem. – Asian J.*, 2013, **8**, 1910; (d) L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, New York, 3rd edn, 1960.
- 13 D. J. Nelson, F. Nahra, S. R. Patrick, D. B. Cordes, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2014, **33**, 3640.
- 14 (a) P. A. Chase and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2008, **47**, 7433; (b) D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones and M. Tamm, *Angew. Chem., Int. Ed.*, 2008, **47**, 7428; (c) D. Holschumacher, C. Taouss, T. Bannenberg, C. G. Hrib, C. G. Daniliuc, P. G. Jones and M. Tamm, *Dalton Trans.*, 2009, 6927; (d) S. Kronig, E. Theuergarten, D. Holschumacher, T. Bannenberg, C. G. Daniliuc, P. G. Jones and M. Tamm, *Inorg. Chem.*, 2011, **50**, 7344; (e) E. L. Kolychev, T. Bannenberg, M. Freytag, C. G. Daniliuc, P. G. Jones and M. Tamm, *Chem. – Eur. J.*, 2012, **18**, 16938.
- 15 A. D. Phillips and P. P. Power, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2005, **61**, o291.
- 16 (a) A. C. Hillier, W. J. Sommer, B. S. Yong, J. L. Petersen, L. Cavallo and S. P. Nolan, *Organometallics*, 2003, **22**, 4322; (b) A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano and L. Cavallo, *Eur. J. Inorg. Chem.*, 2009, **2009**, 1759.
- 17 H. Clavier and S. P. Nolan, *Chem. Commun.*, 2010, **46**, 841.
- 18 G. Giordano, R. H. Crabtree, R. M. Heintz, D. Forster and D. E. Morris, *Inorg. Synth.*, 2007, **19**, 88.
- 19 J. A. McCleverty, G. Wilkinson, L. G. Lipson, M. L. Maddox and H. D. Kaesz, *Inorg. Synth.*, 1966, **8**, 84.
- 20 H. J. Frohn, N. Y. Adonin, V. V. Bardin and V. F. Starichenko, *Z. Anorg. Allg. Chem.*, 2002, **628**, 2827.
- 21 F. A. Cotton, R. L. Luck and K.-A. Son, *Inorg. Chim. Acta*, 1991, **179**, 11.
- 22 Bruker AXS Inc, Madison USA, 2006.
- 23 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1990, **46**, 467.
- 24 G. M. Sheldrick, Universität Göttingen, Göttingen Germany, 1999.
- 25 B. V. Nonius, Delft, The Netherlands, 1997.
- 26 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

